

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P33

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CH₂OO + hν → products

Primary photochemical transitions

Reaction	$\Delta H^\circ_{298}/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CH ₂ OO + hν → CH ₂ O + O(³ P) (1)	185	645
→ CH ₂ O + O(¹ D) (2)	292	410

Absorption cross-section data

Wavelength range/nm	Reference	Comments
280-410	Beames et al., 2012	(a)
300-445	Sheps 2013	(b)
280-500	Ting et al., 2014	(c)
375	Buras et al., 2014	(d)

Comments

- (a) CH₂OO prepared by PLP (248 nm) of CH₂I₂ in O₂/Ar mixtures in a capillary tube. The photoproducts were cooled in a supersonic expansion and passed to a TOF mass spectrometer where they were ionised with VUV radiation at 118nm. The signal at *m/z* 46 detected when 248 nm photolysis occurred in the capillary, was attributed to CH₂OO. The UV absorption spectrum was determined from depletion of the *m/z* 46 photo-ionisation signal resulting from excitation of the B ← X transition in ground state CH₂OO molecules by tunable UV radiation (280 – 420 nm) Nd-YAG laser. The spectrum in this region showed a simple Gaussian form. The maximum absorption cross section of $\sigma = 5 \times 10^{-17} \text{ cm}^2$ at 335 nm.
- (b) CH₂OO prepared by PLP (266 nm) of CH₂I₂ in O₂/Ar mixtures at 5.1 Torr pressure. Absorption of CH₂OO in presence of excess SO₂ was observed by time-resolved UV absorption spectrum at. Chemical kinetics measurements of its reactivity establish the identity of the absorb-

ing species as CH₂OO. Separate measurements of the initial CH₂I radical concentration were used to determine the absolute absorption cross section of CH₂OO. The value obtained at the observed peak of the absorption band, 355 nm, was $\sigma = (3.6 \pm 0.9) \times 10^{-17} \text{ cm}^2$. The difference between the absorption and action spectra was attributed to excitation to long-lived $\tilde{B} (^1A')$ vibrational states that may relax to lower electronic states by fluorescence or nonradiative processes. Spectral resolution was $\sim 1 \text{ nm}$.

- (c) CH₂OO was prepared by pulsed 248 nm photolysis of CH₂I₂/O₂ mixtures; transient absorption spectra were recorded using a gated intensified CCD camera (1 ms gate width) after the probe light was dispersed using a grating monochromator. Spectral resolution was 2 nm. Decay of CH₂OO by self-reaction and by reaction with SO₂ were utilized to extract the absorption spectrum of CH₂OO, corrected for contributions by other absorbers, under reaction conditions. The peak cross section is $(1.26 \pm 0.25) \times 10^{-17} \text{ cm}^2$ at 340 nm, based on the quantum efficiency of CH₂OO production ($\phi_{\text{CH}_2\text{OO}} = 0.86$ at 11 Torr, reported by Stone et al. (2013)). Absolute absorption cross-sections of CH₂OO were also obtained from laser-depletion measurements in a jet-cooled molecular beam. The laser fluence was calibrated with a reference molecule. The values obtained at 308.4 and 351.8 nm were: $(8.09 \pm 0.90) \times 10^{-18} \text{ cm}^2$ and $(1.21 \pm 0.13) \times 10^{-17} \text{ cm}^2$ respectively are consistent with the absorption measurements, taking into account uncertainties in spectral overlap at different resolution and gas temperature.
- (d) CH₂OO was produced by the reaction of CH₂I + O₂ → CH₂OO + I following 355nm laser photolysis of CH₂I₂ ($4 \times 10^{13} \text{ cm}^{-3}$) in a large excess of O₂. CH₂OO kinetics was followed by time resolved absorption at 375 nm in the B ← X transition and the atomic I co-product followed by probing the 1315.246 nm F = 3 ²P_{1/2} ← F = 4 ²P_{3/2} atomic transition. [CH₂OO]₀ determined by fitting simultaneous decay of [I] and [CH₂OO]. The absorption cross section of CH₂OO at the UV probe wavelength ($\lambda = 375 \text{ nm}$) was derived as $(6.2 \pm 2.2) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. in good agreement with very recent measurement of Ting et al. ($7.7 \pm 0.385 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 375 nm).

Preferred Values

Absorption cross-sections at 298 K

λ/nm	σ/cm^{-2} $\times 10^{-20}$	λ/nm	σ/cm^{-2} $\times 10^{-20}$	λ/nm	σ/cm^{-2} $\times 10^{-20}$
280	190	340	1230	400	345
285	290	345	1215	405	190
290	380	350	1200	410	230
295	490	355	1125	415	110
300	551	360	1050	420	120
305	660	365	1004	425	45
310	785	370	844	430	50
315	920	375	767	435	30
320	979	380	720	440	0
325	1075	385	455	445	0
330	1140	390	520	450	0
335	1195	395	300	455	0

$$\sigma = (1.23 \pm 0.18) \times 10^{-17} \text{ cm}^2 \text{ at } \lambda_{\text{max}} (340 \text{ nm})$$

Quantum Yields

$$\phi_1 = 1.0 \text{ for } 280 < \lambda < 420 \text{ nm.}$$

Comments on Preferred Values

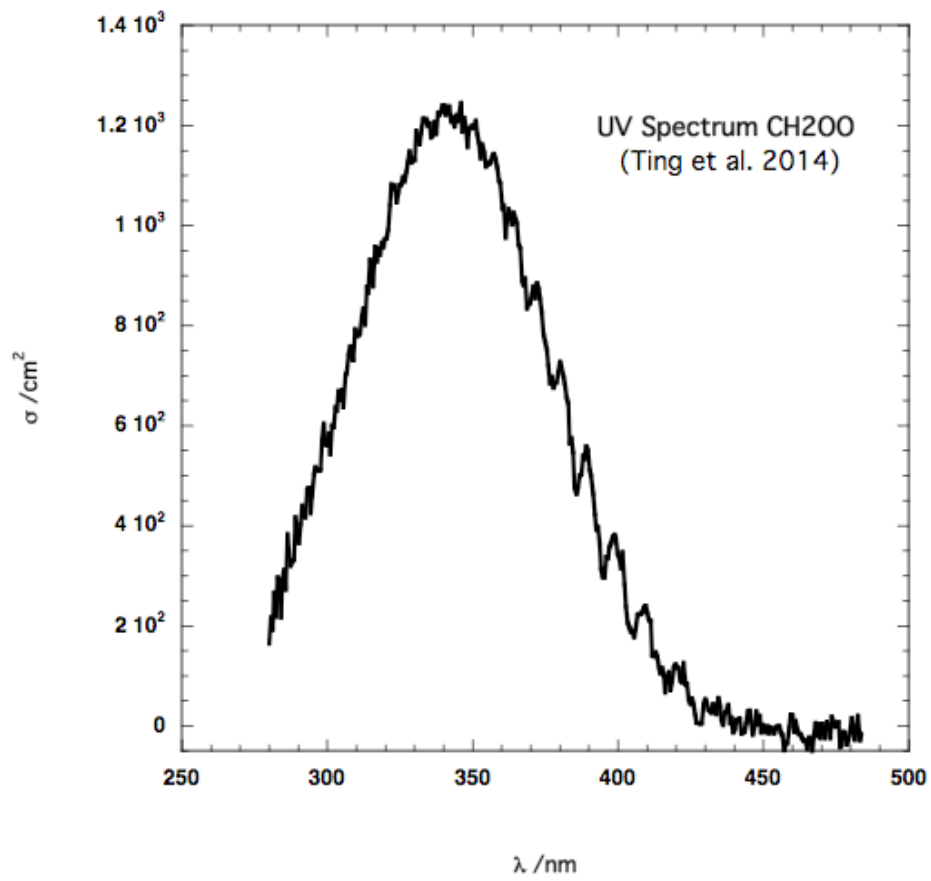
All reported studies of UV absorption by the formaldehyde oxide Creigee diradical show a strong absorption band in the mid UV region which is attributed to the in the $\tilde{B}(1A') \leftarrow \tilde{X}(1A')$ electronic transition. However the results are not all in good agreement, either in absolute magnitude of the cross section at the absorption maximum, or in the overall shape of the spectrum. The UV photo-dissociation action spectrum reported by Beames et al, (2012) differs substantially from the absorption spectrum of formaldehyde oxide reported by Shaps (2013) in that the latter extends to longer wavelengths and exhibits resolved vibrational structure on its low-energy side. The cross-section estimate of Beames et al. was based on a laser fluence estimated without correction for beam non-uniformity. Ting et al (2014), used both multiplex long-path UV absorption and the photo-dissociation action technique, to give improved accuracy to determine cross-sections over a wide range of wavelengths. The results agree well the long wavelength results of Shaps (2013) but there is clear and unexplained conflict with these results at $\lambda < 345 \text{ nm}$, where the absorption falls off much more rapidly. Explanations of the differences in shape based on strong temperature dependence at longer wavelengths (analogy to the Hartley/Huggins bands in

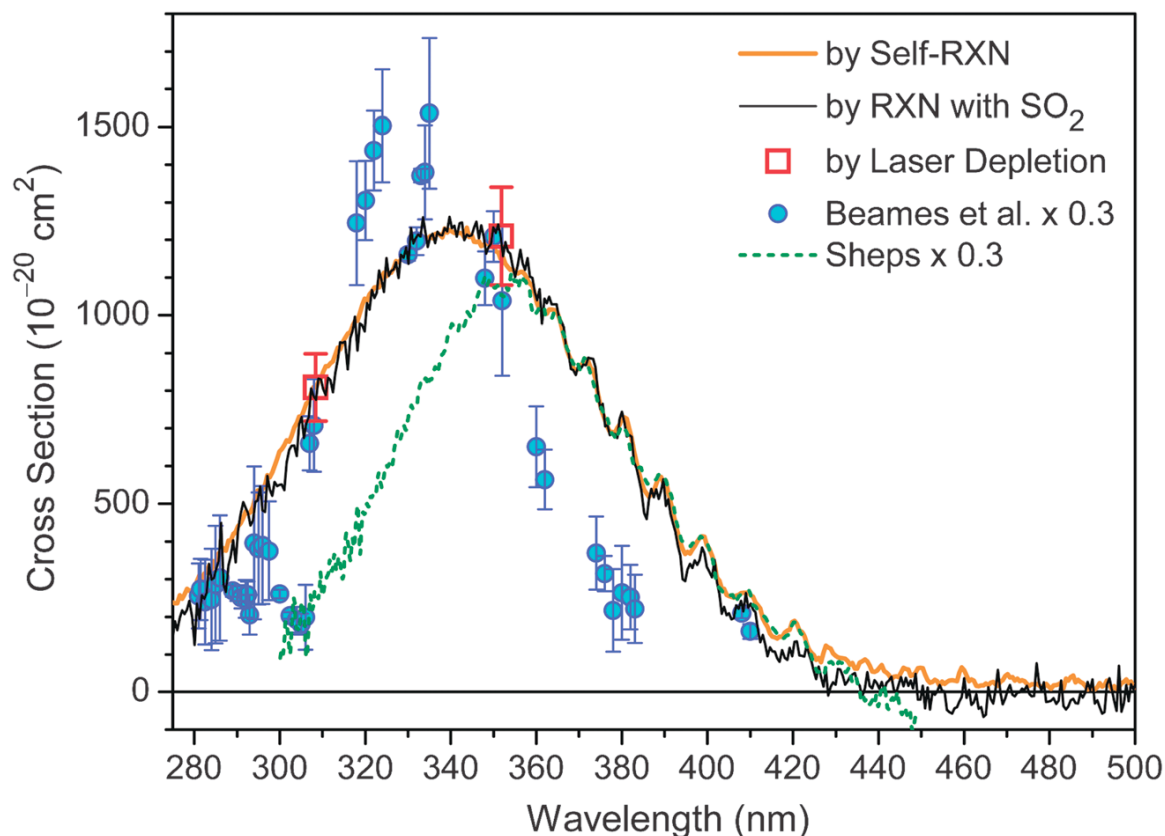
iso-electronic O₃ molecule), and a proposed decrease in the dissociation yield at long wavelengths (Shaps, 2013) due to competing processes are not consistent with the body of photophysical information. The single wavelength determination of σ (375) nm of Buras et al. (2014), as part of their kinetic study of the CH₂OO self reaction, is in good agreement with the results of Ting et al.(2014). The photodissociation quantum yields are likely to be close to unity since the product anisotropy measured by Lehman et al.(2013) shows that dissociation occurs faster than rotation of the CH₂OO molecule.

The preferred value of the cross section at the λ_{\max} in the B-X transition is based on those measured by Ting et al (2014), in their jet cooled measurements, i.e. values obtained at 308.4 and 351.8 nm were: $(8.09 \pm 0.90) \times 10^{-18} \text{ cm}^2$ and $(1.21 \pm 0.13) \times 10^{-17} \text{ cm}^2$ respectively. These values are expected to have very weak temperature dependence by analogy with O₃ Hartley band. The cross-sections at discrete wavelengths over the range 280-500nm were obtained by Ting et al (2014), by scaling their absorption data to the above data points near λ_{\max} . The IUPAC recommended peak cross section at 340 nm and cross-sections at 5nm intervals are evaluated by averaging data from their analysis. The error of $\pm 15\%$ includes possible variations arising from the temperature effects.

References

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Buras, Z.J., Elsamra, R.M.I., and Green, W.H., Chem.Phys.Lett., 5, 2224, 2014.
Sheps, L., J.Phys.Chem.Lett., 4, 4201, 2013.
Ting, W-L, Chen, Y-H., Chao, W., Smith, M.C., and Lin, J Jr -M., Phys. Chem. Chem. Phys., 16, 10438, 2014.
Lehman, J.H., Li, H., Beames, J. M., and Lester, M. I., J.Chem.Phys., 139, 141103, 2013





Absorption spectrum of CH₂OO. The thick orange and thin black lines are the average curves of Fig. 2a and b, respectively from Ting et al.(2014). For the thin black line (numerical values can be found in ESI† of their publication). The absorbance due to the reacted SO₂ has been removed, based on the mass balance of (R2) (see ESI†). The black and orange lines are scaled to match the absolute cross section at 340 nm. Red square symbols are the absolute cross sections from the molecular beam-laser depletion measurements (Ting et al., 2014, Table 1). The results of Sheps (2013) and Beames et al.(2012) are scaled by a factor of 0.3 for easier comparison. The temperature of the photolysis cell was 295 K. The molecular beams of this work and Beames et al. were jet-cooled (estimated rotational temperature 10 K).

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